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Esomeprazole Magnesium Trihydrate Drug as a Potential Non-Toxic Corrosion Inhibitor for Mild Steel in Acidic Media

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ABSTRACT

The inhibiting effect of Esomeprazole magnesium trihydrate drug on the corrosion of mild steel (MS) in 1 M HCl was performed by chemical tests (weight loss (WL)) and electrochemical methods (Tafel polarization (TP), electrochemical frequency modulation (EFM) and AC impedance spectroscopy (EIS)). The adsorption isotherm of Esomeprazole Mg Trihydrate drug on the MS surface was found to follow Temkin adsorption isotherm. Some thermodynamic parameters were computed and discussed. The obtained data showed that the inhibition efficiency (IE) rises with increasing the dose of the Esomeprazole Mg Trihydrate and with raising the temperature. The morphology of MS surface was analyzed by using scanning electron microscope (SEM) and atomic force microscopy (AFM) techniques. Fourier transforms infrared spectroscopy (FTIR). All test methods gave corresponding results

Keywords: Acid corrosion; Mild steel; SEM; AFM; FTIR; Esomeprazole magnesium trihydrate

INTRODUCTION

Corrosion is an essential procedure playing a significant role in safety and economics , particularly for metals [1]. MS corrosion causes short shelf life, safety issues (hydrogen gas evolution), self-discharge and loss of valuable capacity, to reduce these undesirable effects, MS corrosion must be controlled [2]. Numerous inhibitors in utilized are either synthesized from cheap raw material or chosen from composite having heteroatoms in their aromatic or long-chain carbon system [3-4]. The studies prove that the inhibition influence of these organic composite occurring by its adsorption on surface of MS. Organic heterocyclic composite have utilized for the corrosion inhibition of CS [5-10], copper [11], aluminum [12-14], and other metals [15] in altered aqueous solution. The drug adsorbed assisted to protect the metal surface [16]. The select of some medication for inhibitor of corrosion is taking due to contain active centers, ecofriendly environmentally and simply purified and formed [17]. In recent years, the drugs were utilized as corrosion inhibitors for different metals as result to their high solubility in water, with high molecular size and containing electronegative atoms such as N, O S atoms in their molecules and nontoxic nature such these compounds should be good corrosion inhibitors [18-19]. Adsorption of the drug molecules on the metal surface facilitates its inhibition [20-31].

The scope of this paper is to examine the inhibitive effect of Esomeprazole magnesium trihydrate towards the corrosion of MS in 1M HCl utilizing electrochemical and non-electrochemical tests. The surface examination of the MS specimens was also analyzed.

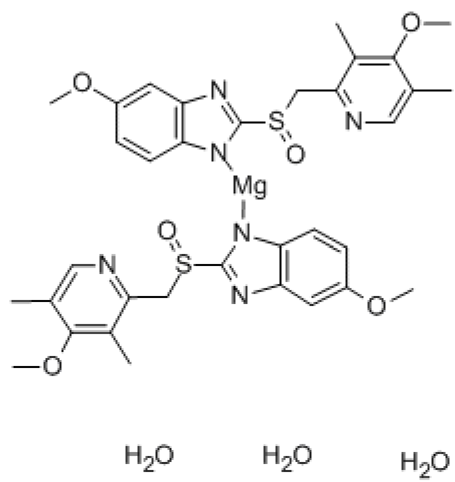
MATERIALS AND METHODS

Metal Sample

MS contain of iron alloyed with less than 0.3 % C, most commonly among 0.1 to 0.25 %. The building industry always utilized MS in construction due to its ductility and malleability (Fe=99.77% C= 0.06495).

Chemicals

Inhibitor – Esomeprazole magnesium trihydrate is the investigated drug which has been used as inhibitor. Absolute ethanol (99 %) were supplied from Gamhoria Company and used for the preparation of ethanolic-aqueous mixtures with bi-distilled water (Figure 1).



Scheme 1. Magnesium;5-methoxy-2-[(4-methoxy-3,5-dimethylpyridin-2-yl)methylsulfinyl]benzimidazol-1-ide;trihydrate

$C_{34}H_{42}MgN_6O_9S_2$

M.Wt=767.168 g/mol

Solutions

The aggressive solution 1M HCl. Solutions of Esomeprazole magnesium trihydrate in ethanol-water mixed solvents with different ethanol mole fractions ($x1$=0 to 1.0 by weight) were prepared for density and refractive index measurements.

WL Measurements

For WL tests, square coins of surface area 2.6 x 2.8 cm were exposed to the corrosive medium for 3 h. The coins have abraded with emery papers with grit sizes (250,600 and 2000) and cleaned with acetone and finally dried by filter papers. The WL tests have taken in 100 mL glass beaker. The coins were then immediately immersed in the test solution with and without various doses of the investigated drug and all dipped in a water thermostat. The average WL for MS coins will achieve. The (%IE) and the (θ) of Esomeprazole Mg Tri hydrate for the corrosion of MS were measured as next [32]:

$$\% IE=\theta \times 100=[1-(W/W^0)] \times 100 \quad (1)$$

where W^0 and W are the WL with and without adding various doses of investigate drug, correspondingly.

Electrochemical Measurements

PP method was taken in a typical three compartments glass cell [33].The potential range was (-800 to +200 mV vs. SCE) at OCP with a scan rate 1 mVs^{-1}. Then i_{corr} was calculated for the measurements and was used to calculate the %IE and the θ from Eq. (2) as below:

$$IE \%=\theta \times 100=[1-(i_{corr(inh)}/i_{corr(free)})] \times 100 \quad (2)$$

where $i_{corr(free)}$ and $i_{corr(inh)}$ are the current densities in the absence and presence of Esomeprazole Mg Tri hydrate, correspondingly.

Impedance measurements were done by AC signs of 10 mV peak-to-peak amplitude and at a range of frequency of 10^7 Hz to 0.1Hz [34]. The capacitance of the double layer C_{dl} , (% IE) and θ were founded from eqns. (3) and (4) which are defined as:

$$C_{dl}=1/(2 \pi f_{max} R_{ct} \quad (3)$$

where f_{max} is the maximum frequency

$$IE \%=\theta \times 100=[1-(R°_{ct}/R_{ct})] \times 100 \quad (4)$$

where R^o_{ct} and R_{ct} are the charge transfer resistances without and with drug, respectively.

EFM technique used two frequencies of range 2 and 5 Hz depending on three conditions. The (i_{corr}), (β_c and β_a) and (CF-2, CF-3) (Causality factors) [35] were measured by the higher two peaks.The % IE_{EFM} was calculated as in eqn. (2)

(TP), (EFM) and (EIS) techniques were performed utilizing the similar manner as earlier with a Gamry framework system rely on ESA400. Gamry apparatus includes software EFM140 for EFM tests and EIS300 for EIS method; the computer has used for summation value. Echem Analyst 5.5 Software hadutilized for drawing and fitting data.

Surface Examinations

The MS coins utilized for analysis of morphology surface were set in 1M HCl acid (blank) and in presence of 30 ppm of Esomeprazole Mg Tri hydrate at room temperature for one day after abraded mechanically utilizing various emery papers up to 1200 grit size. Then, after this exposure time, the examination was carried out by utilizing (SEM), AFM and FTIR tests.

RESULTS AND DISCUSSION

Weight Loss (WL) Measurement

Weight loss of MS, in mg cm^{-2} of the surface area, was measured at different time periods with and without various doses (10- 60 ppm) of the Esomeprazole magnesium trihydrate. The curves obtained with different doses of drug fall considerably below that of free acid as shown in Figure 1. The % IE's are recorded in Table 1. In all cases, the efficiency of the drug was improved with raising doses of the Esomeprazole magnesium trihydrate and the rate of corrosion was lowered. These results indicated that, the Esomeprazole magnesium trihydrate is good efficient inhibitor for MS dissolution in HCl solution.

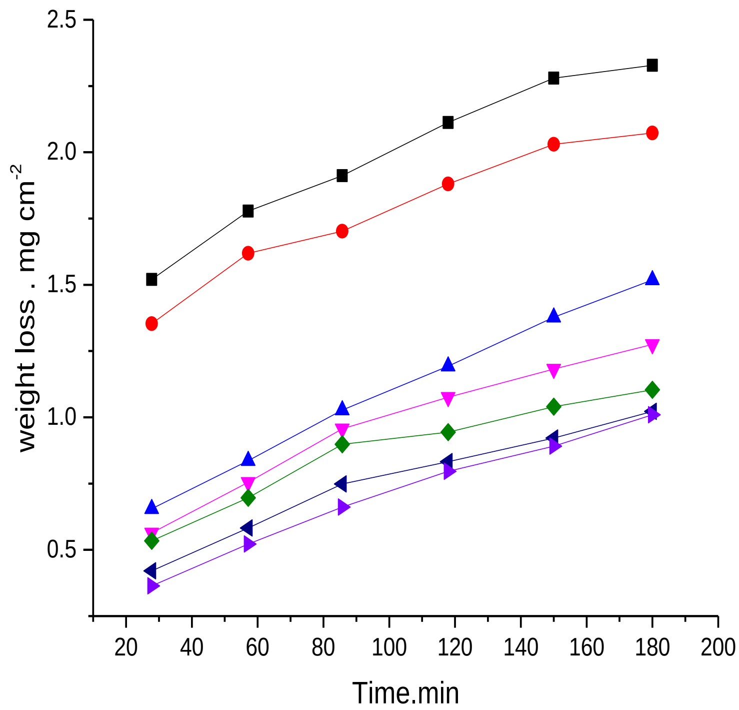


Figure 1. WL-time diagrams for the MS in 0.5 M HCl without and with various doses of Esomeprazole magnesium trihydrate at 25°C

Table 1. %IE of different doses of Esomeprazole magnesium trihydrate at different temperatures after 120 min exposed in 1 M HCl solution

Conc., ppm	**%IE**				
	25°C	**35°C**	**45°C**	**55°C**	**65°C**
10	30.9	77.5	80.2	83.6	85.5
20	48.0	79.8	82.5	87.4	91.6
30	49.0	80.7	83.4	88.2	91.7
40	55.3	82.2	85.2	90.1	92.2
50	60.5	82.8	87.8	91.5	93.4
60	68.0	85.4	89.4	92.0	93.2

Adsorption Isotherms

The adsorption isotherms were used to explain the adsorption mechanism of the inhibitors on the metal surfaces. The best fitting isotherm for our data is the Temkin isotherm. Figure 2 shows the plotting of θ against log C at 25°C for Esomeprazole magnesium trihydrate drug. This plot gave straight lines indicating that the adsorption of Esomeprazole magnesium trihydrate on MS surface obeys Temkin isotherm:

$$\Theta=(1/f)\ \ln K_{ads}\ C \qquad (6)$$

$C_{inh}$is the inhibitor dose, K_{ads} is the adsorption equilibrium constant, and "a" is a parameter of lateral interaction which describes the molecular interactions in the adsorbed layer

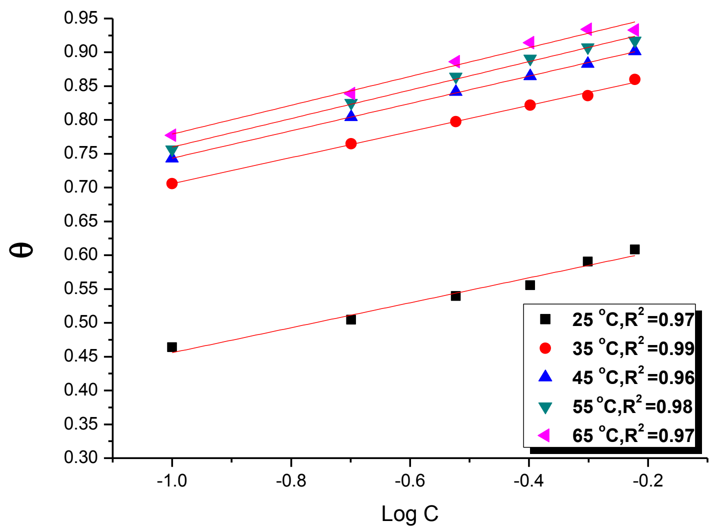


Figure 2. Temkin curves of Esomeprazole magnesium trihydrate on MS in HCl at various temperatures

Table 2. Temkin adsorption isotherm of Esomeprazole magnesium trihydrate drug on MS surface in 1 M HCl at various temperatures

Temp °C	a	$-\Delta G^o_{ads}$, *kJ mol⁻¹*	ΔH^o_{ads} *kJ mol⁻¹*	ΔS^o_{ads} *J mol⁻¹ K⁻¹*
25	12.5	29.7	49	99
35	11.9	35.3		114
45	10.8	36.6		115
55	10.9	39.6		120
65	10.5	40.8		121

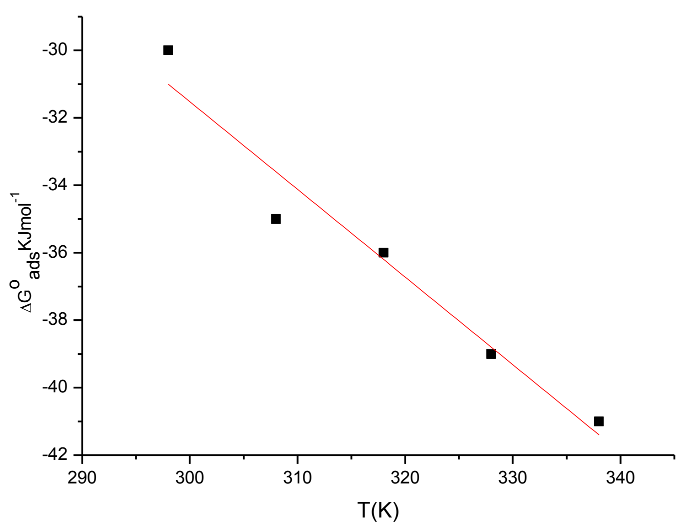


Figure 3. ΔG°_{ads} vs (T) for corrosion of MS in 1M HCl in the presence of Esomeprazole magnesium trihydrate

As reported in the literature if the value of ΔG^o_{ads} is between -20 and -40 kJ mol^{-1}the adsorption of the inhibitor on the metal surface is mixed one (i.e.physisorption and chemisorption). So the adsorption of the investigated drug on

MS surface is mixed one (ΔG^o_{ads}, between -20 and -40 kJ mol^{-1}). The negative sign data of $\Delta G°_{ads}$ means that adsorption occurs spontaneously. The standard enthalpy $\Delta H°_{ads}$ and $\Delta S°_{ads}$ can be measured using the following Eq. (7):

$$\Delta G^{\circ}_{ads}=\Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \qquad (7)$$

The $\Delta H°_{ads}$ data was evaluated from the intercept of the plot of ΔG°_{ads} versus T (Figure 3). The positive sign data of $\Delta H°_{ads}$ ensures that the process of adsorption is an endothermic, the ΔS^o_{ads} obtained from the slope of the line of Fig.3. The negative sign on ΔS^o_{ads} indicates that the adsorption of the drug accompany by ordering of the drug on the MS surface.

Effect of Temperature

WL tests were used to prove the temperature effect on MS corrosion rate (k_{corr}) in Aggressive solution. Figure 1 showsWL of MSin corrosive solution with many Esomeprazole Mg Trihydrate doses at various temperatures (298–338K). Table 1 illustrate the adsorption is aided by raising the temperature. This performancedemonstrates that the adsorption of inhibitors on MS surface happens among chemical adsorption. Ivanov [36], considers the rise of %IE with temperature rise, MS chemisorption is preferred as higher temperature. Other authors [37-39] reported similar explanations.

Kinetic–Thermodynamic Corrosion Parameter

Activation energies for corrosion process (E^*_a) were obtained from Arrhenius relation as follows:

$$\log k_{\mathbf{corr}}=\log A - (E^*_a / 2.303R) (1/T) \qquad (8)$$

where A is constant, R is universal gas constant, and T is temperature in Kelvin [40-43]. Plots of log k_{corr} and 1000/T were illustrated in Figure 4. Enthalpy of activation for the corrosion process (ΔH^*) and entropy of activation for corrosion process (ΔS^*) were determined by plotting log k_{corr}/T against 1/T (Figure 5), according to the following equation:

$$\log k_{corr}/T =\log (R/ Nh + \Delta S^*/ 2.303R) + (-\Delta H^*/ 2.303R) (1/ T) \qquad (9)$$

where h is constant and N is number of Avogadro. Increasing of E^*_a and $\Delta H^*$with Esomeprazole magnesium trihydrate was because energy barrier that created in existence of Esomeprazole magnesium trihydrate. ΔH^* values were found to have positive signs, indicating anodic dissolution reaction of MS. Negative ΔS^*indicated that from reactants to the activated complex, the disorder lowered [44].

Figure 5 shows a plot of (log k_{corr}) against (1/T) in the case of inhibitor Esomeprazole magnesium trihydrate in 1 M HCl. A straight line is obtained with a slope equals to (ΔH^*/2.303R) and the intercept is [log (R/Nh + ΔS^*/2.303R)] are calculated (Table 3).

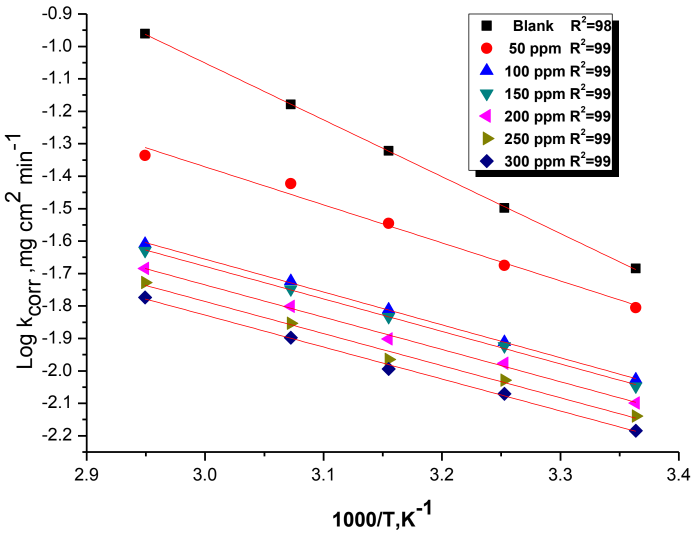


Figure 4. (log k_{corr}/T) against (1000/T) in 1.0 M HCl without and with various doses of drug

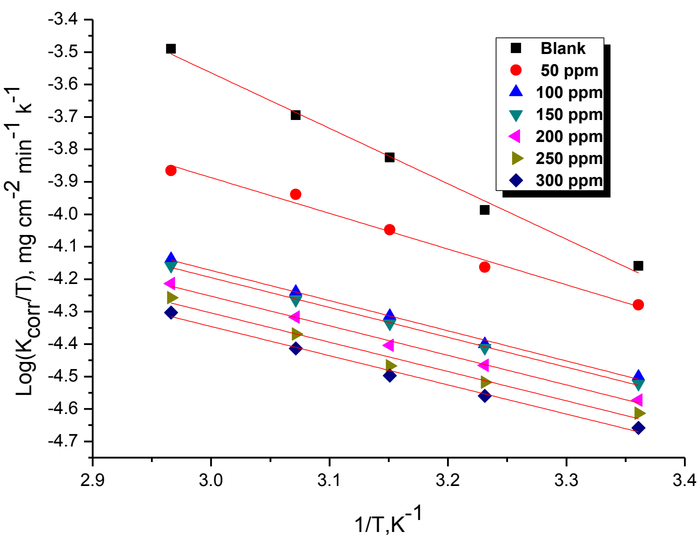


Figure 5. Log (k_{corr}/T) vs (1000/T) curves for MS immersed in 1 M HCl with and without various doses of the drug

Table 3. Parameters from activation process for MS in corrosive solution without and with various drug doses

$C_{inh.}$ ppm	Activation parameters		
	E_a^* (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	$-\Delta S^*$ (J mol^{-1}K^{-1})

blank	58.8	32.7	167.5
10	22.4	21.1	208
20	19.3	17.7	223
30	19.1	17.6	224
40	19.0	17.4	226
50	18.9	17.2	228
60	18.8	17.2	229

Electrochemical Frequency Modulation (EFM) Measurements

EFM is characterized by speed and greatly accuracy in calculating the current data [45]. Figure 6 indicate the EFM of MS in 1 M HCl solution and at 30 ppm of Esomeprazole magnesium trihydrate drug. The EFM parameters such as (CF-2 and CF-3), (β_c and β_a) and (i_{corr}) can be measured from the higher current peaks. The CF is closer to the standard data proved the validity of the calculated data (Table 4). The IE% increase with the raising of Esomeprazole Mg Trihydrate doses. The % IE_{EFM} rise by raising the drug doses and was measured as in eqn. (2)

Table 4. Parameters of EFM diagrams for MS corrosion without and with various doses of the drug in 1 M HCl at 25ºC

	i_{corr} uA	**β_a mV/deade**	**β_c mV/dec**	**CR mpy**	**CF2**	**CF3**	**ϴ**	**%IE**
blank	420.4	86	92	192.10	1.7	2.7		
5	186	114	126	49	2.90	1.50	0.557	55.7
10	172.2	107	121	57.80	2.27	1.90	0.59	59
15	114.1	110	12.3	57.1	2.80	2.40	0.728	72.8
20	98.76	82	879	45.02	2.21	1.89	0.765	76.5
25	81.99	71	735	43.20	2.47	1.98	0.728	72.8
30	57.67	56	59.1	39.91	2.07	2.19	0.805	80.5

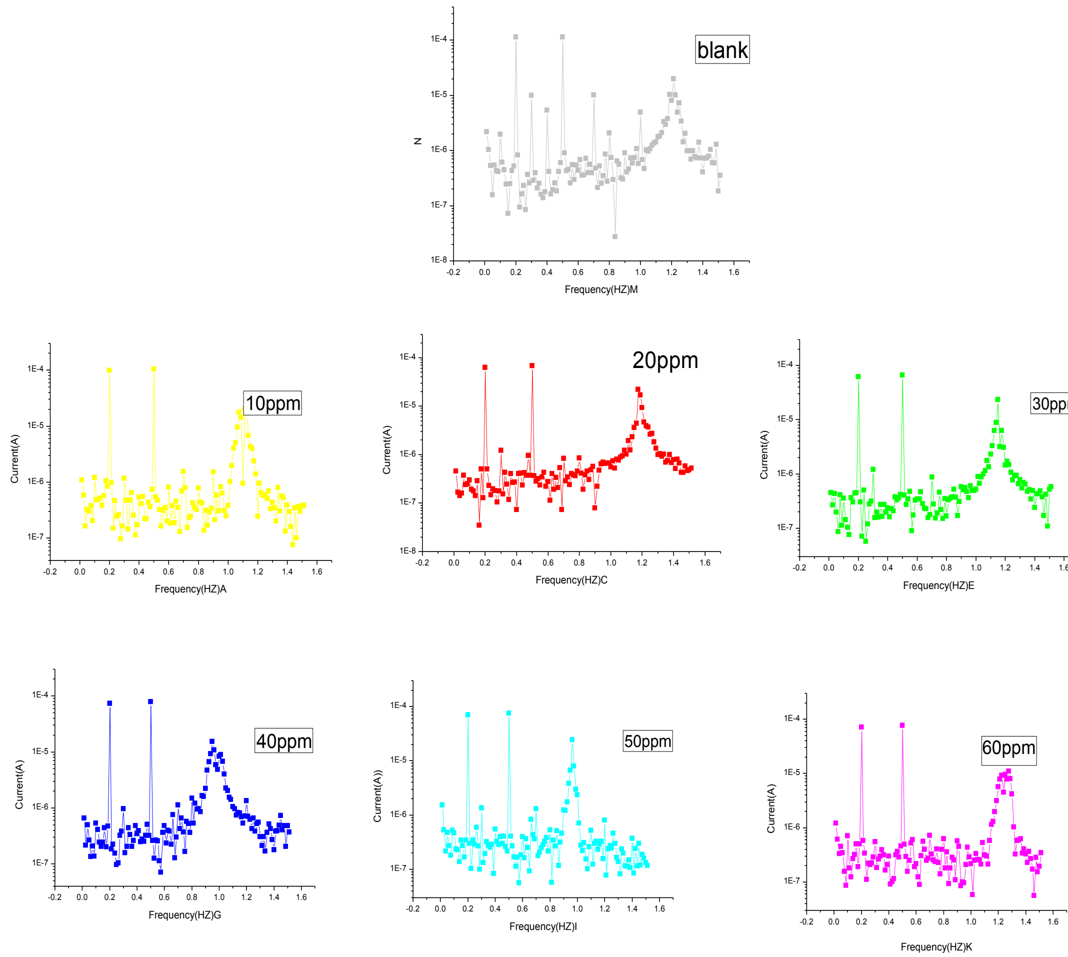


Figure 6. EFM spectra for MS in 1 M HCl (blank) and the presence of various doses of the drug

Electrochemical Impedance Spectroscopy (EIS) Measurements

Both Nyquist and Bode bends for MS corrosion in 1 M HCl only and also in acid in existence of varied dose of Esomeprazole magnesium trihydrate were obtained by EIS procedure and shown in Figure 7a and 7b). It is noticed from Nyquist figure that the curves appear semicircular. The frequency dispersion is responsible for the shape of the curve. The special shape of the Nyquist curves confirms that the MS corrosion is controlled by charge transfer process [46,47].It was found that in the Nyquist diagrams the existence of inhibitor leads to raise the diameter of capacitive loop. Charge transfer resistance (R_{ct}) is responsible for high frequency capacitive loop. The double layer capacitance (C_{dl}) is the frequency at which the component of the impedance is maximum and could be measured according to the next balance.

$$C_{dl}=1 / 2 \pi F_{max} R_{ct} \quad (10)$$

Where R_{ct} is the charge transfer resistance and f is the frequency at the maximum altitude of the semicircle. The parameters obtained by EIS procedure was report in (Table 5). From the results calculated, it was observe that the

R_{ct} values increases with increasing Esomeprazole Mg Tri hydrate dose but C_{dl} data lowered. The adsorption of Esomeprazole magnesium trihydrate on the MS surface leads to this result. The results obtain proves that the Esomeprazole magnesium trihydrate works by forming the protective layer on the MS surface which modifies the MS/acid interface.

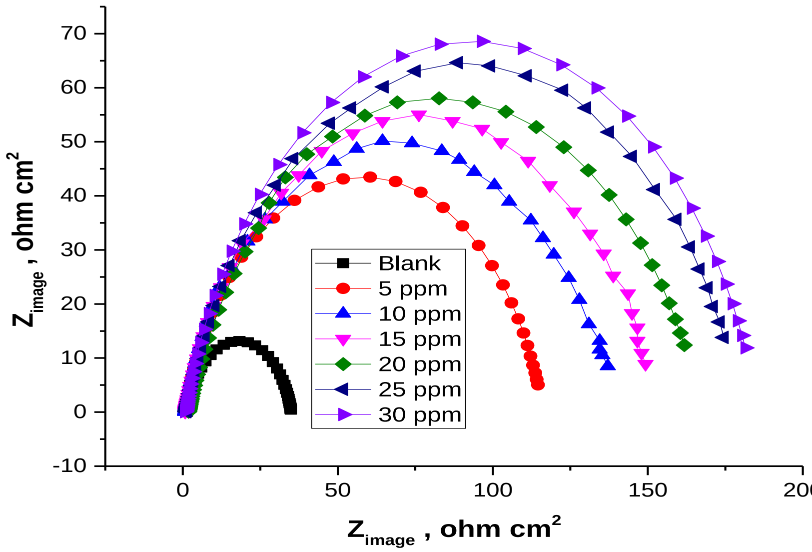


Figure 7a. Nyquist plots for the MS corrosion in 1M HCl with and without various doses of the drug at 25°C

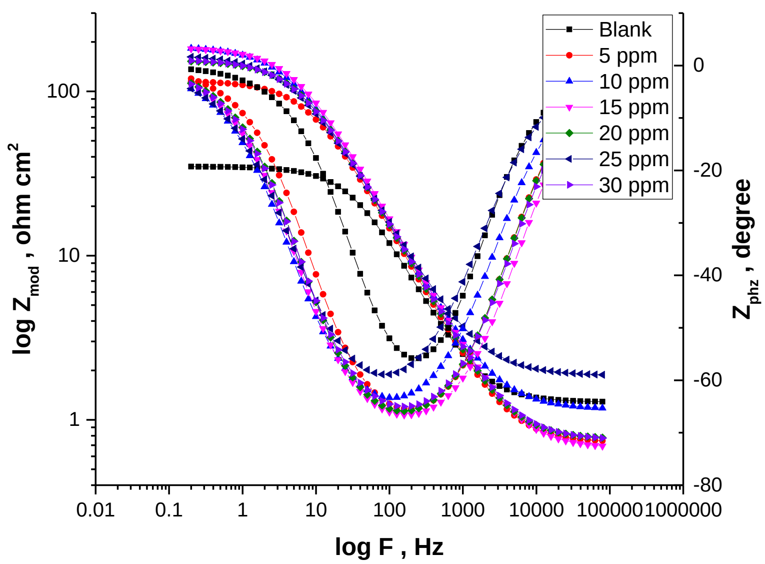


Figure 7b. The Bode plots for the corrosion of MS in 1M HCl with and without various doses of Esomeprazole magnesium trihydrate at 25°C

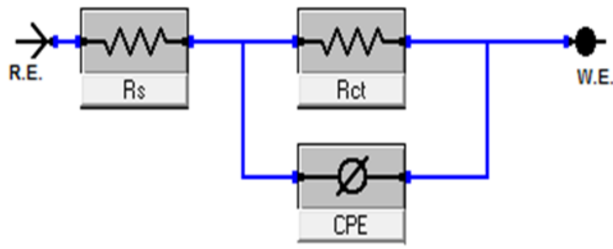


Figure 8. Circuit applied to fit the impedance data

Table 5. The obtained data from EIS tests for MS in 1M HCl with and without various doses of Esomeprazole magnesium trihydrate

Conc., ppm	R_{ct}, ohm cm^2	C_{dl}	Ɵ	IE%
blank	33.7	237	-----	-----
5	115.4	200	0.708	70.8
10	154.8	191	0.782	78.2
15	156.4	176	0.785	78.5
20	165.6	172	0.796	79.6
25	185.3	165	0.818	81.8
30	187.3	162	0.820	82.0

Tafel Polarization (TP) Measurements

Figures 8 and 9 shows Tafel plots at 25^{o}C for MS in corrosive solution without and with many Esomeprazole magnesium trihydrate concentrations. As indicated from the figure, increasing Esomeprazole Mg Tri hydrate concentration leads to decrease cathodic "H_2 reduction" and anodic "metal dissolution" reactions. This behavior illustrated that a mixed type inhibitor mechanisms are present. %IE and θ from TP tests were calculated using Eq. (2). Table 6shows the determined values of $i_{corr.}$, $E_{corr.}$, Tafel slopes (β_a and β_c), k_{corr}, θ and %IE. The data indicated that i_{corr} decreased with raising Esomeprazole magnesium trihydrate dose and β_a& β_c remained almost unchanged with addition of Esomeprazole magnesium trihydrate, indicating that the adsorbed inhibitor decreases k_{corr} without affecting the reaction mechanism.

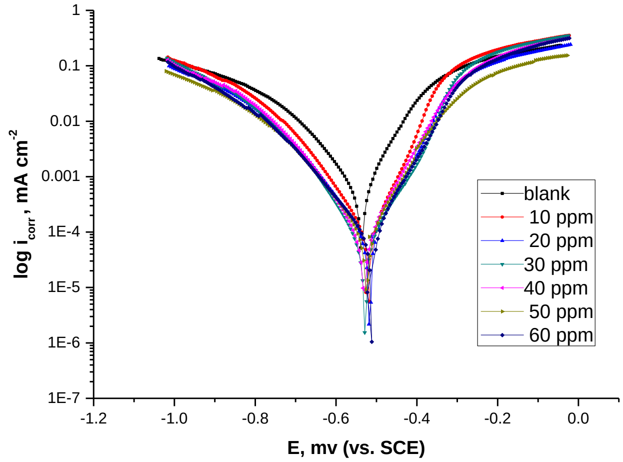


Figure 9. Tafel plots for CS in corrosive solution without and with different doses of the drug at 25°C

Table 6. i_{corr}, E_{corr}, β_c, β_a, k_{corr}, θ, and %IE for CS in the corrosive solution without and with different doses of the drug

Conc., ppm	i_{corr} µA cm^{-2}	$-E_{corr}$ mV vs SCE	β_a mV dec^{-1}	β_c mV dec^{-1}	C R mpy	Ө	%IE
blank	542.0	573	81	118	261.7	----	----
5	92.8	542	85	115	42.4	0.829	82.9
10	86.2	530	82	110	39.4	0.841	84.1
15	62.9	518	74	105	28.7	0.884	88.4
20	55.7	529	84	103	25.4	0.897	89.7
25	41.3	512	68	108	18.8	0.924	92.4
30	35.8	521	54	74	16.3	0.934	93.4

SEM Analysis

Figure 10a-c shows different SEM micrographs of MS samples. Figure 10a shows free MS. Figure 10b shows MS in corrosive solution. Figure 10c shows CS in corrosive solution + 30 ppm Esomeprazole Mg Tri hydrate. The presence of MS in the acidic medium (Figure 10b) leads to genesis of pits, cracks, and corrosion products on the surface. Presence of Esomeprazole Mg Tri hydrate in the solution (Figure 10c) minimizes that pits, cracks and corrosion products and makes the surface smoother. This might be due to formation of a passive layer through Esomeprazole Mg Tri hydrate adsorption on the MS surface that blocks the active sites and minimizes metal contact with corrosive solution.

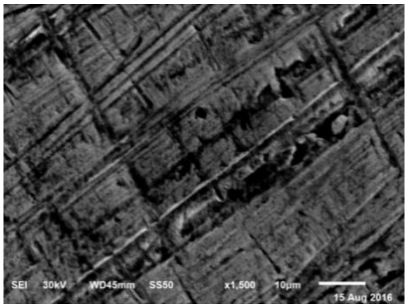
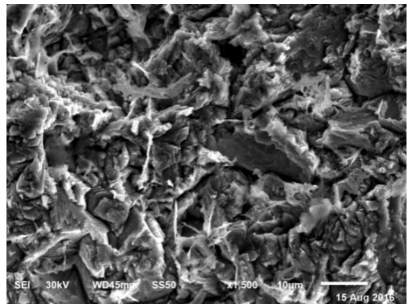
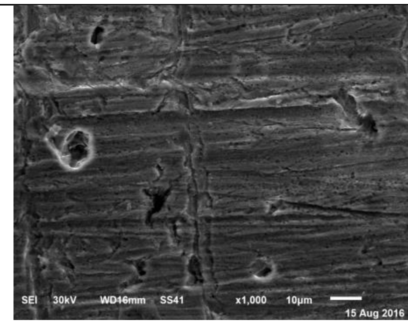
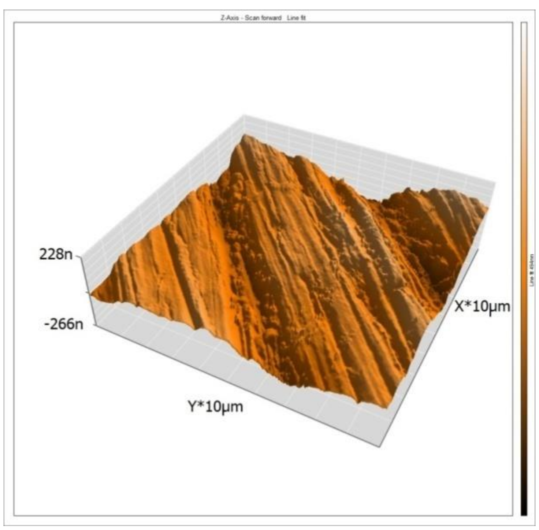
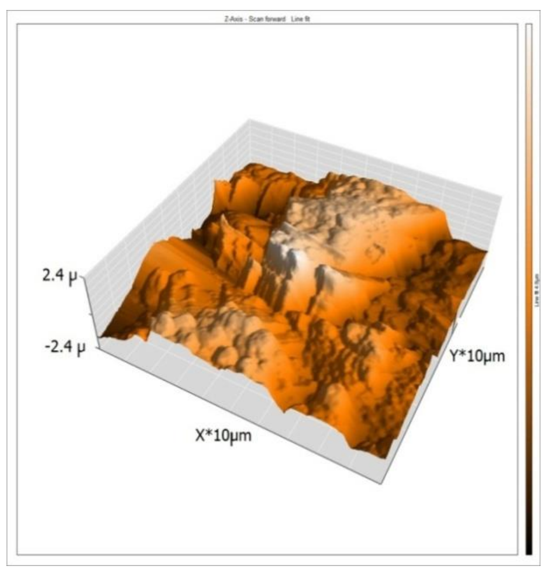
		
(a) **Free sample**	**(b)** **Blank**	**(c)** **1M HCl + 30ppm of** **Esomeprazole Mg Tri hydrate**

Figure. 10. SEM micrographs for MS with and without of 30 ppm of drug after immersion for one day

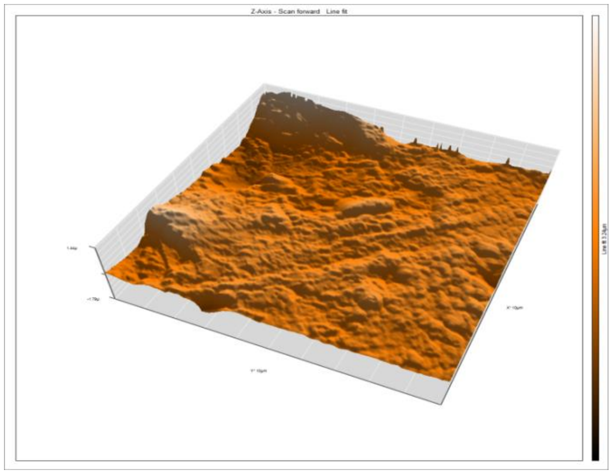
Atomic Force Microscopy (AFM) Analysis

AFM is a remarkable technique used for measuring the surface roughness with high resolution. Many details about MS surface morphology can be obtained from AFM measurements which help explaining the corrosion process. The three dimensional AFM images were represented in Figure 11.





(a) Free **(b) Blank**



(**c) Inhibitor**

Figure 11. The 3D of optical images of AFM in free sample of metal (a) and blank (b) and Esomeprazole magnesium trihydrate inhibitor (c)

The mean roughness is given (553 nm) for the blank in acid solution which putted in 1M HCl for one day and then examined. The observation of the MS surface which dipped in 1M HCl in existence of 30 ppm of Esomeprazole magnesium trihydrate given (332 nm) compared to the blank solution. The values showed that the roughness rises with adding HCl due to the corrosion occurs on the MS surface but decreased with adding the Esomeprazole magnesium trihydrate [48] due to the formation of a film of drug on MS surface.

FTIR Analysis

Figure 12 shows the FTIR spectra of the Esomeprazole magnesium trihydrate drug. The finger print spectra of the drug and the MS surface after immersion in 1M HCl + 60 ppm of Esomeprazole magnesium trihydrate was obtained and compared to each other it was obviously clear that the same finger print of meloxicam stock solution present on MS surface except the absence of some functional group and it suggested to be due to reaction with HCl. From Figure there are small shift in the peaks at MS surface from the original peak of the stock inhibitor solution, these shifts indicate that there is interaction between MS and some of the inhibitor's molecules.

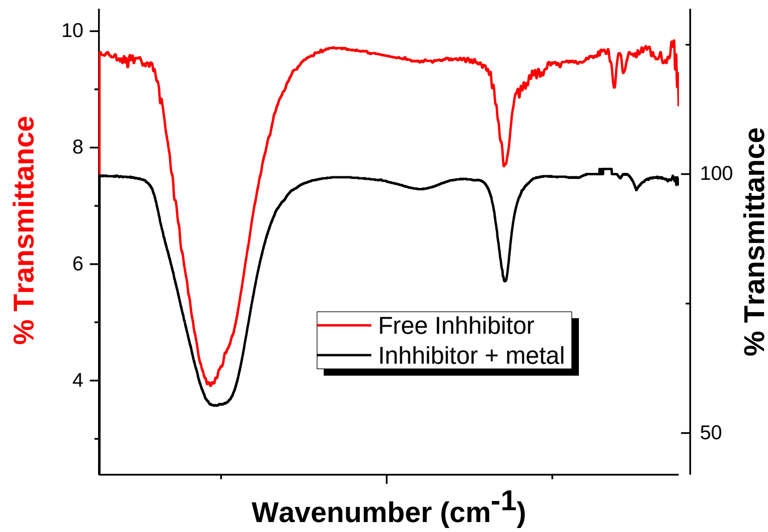


Figure 12. FTIR spectra of the Esomeprazole magnesium trihydrate drug

Mechanism of Corrosion Inhibition

The inhibition mechanism includes the inhibitor adsorption on the MS surface dipped in aqueous HCl. Four natures of adsorption [49] may occurring contain organic molecules at the interface among MS/solution interface: 1) Electrostatic attraction among the charged metal and the charged molecules; 2) Interaction of unshared electron pairs in the molecule through the metal; 3) Interaction of π-electrons with the metal; 4) Summation of all the above. From the observations drawn from the various tests, corrosion protection of MS in 1 N HCl solutions by Esomeprazole magnesium trihydrate as designated from WL, PP and EIS tests were found to rely on the dose and the nature of the protection. Molecules of the Esomeprazole magnesium trihydrate can suppress anodic and cathodic processes either by physisorption or by chemisorption, where interactions of metal and inhibitors may due to electrostatic interaction or electron transfer process, respectively. Moreover, the negative value of ΔG^{o}_{ads} with the range -29.7 to -40.8 kJ mol^{-1} confirms the spontaneous adsorption of the drug on MS surface by both physisorption and chemisorption processes. In the acid medium the drug molecules may be protonated or may be neutral. Physisorption mechanism is due to: In the acid medium the drug molecules are protonated so, there is difficult for these protonated molecules to adsorb on the positive MS surface [50]. Chloride ions get first adsorbed on MS surface, the MS surface becomes negatively charged, and then the protonated Esomeprazole magnesium trihydrate molecules get adsorbed on the chloride layer. Chemisorption mechanism is due to: the neutral molecules can be adsorbed onto the MS surface via electron transfer from adsorbed species to the vacant electron orbital of low energy in the metal to form co-ordinate link.

A comparative study showing IE performance of some of the drugs reported before in the literature is illustrated in Table 7. The present drug shows considerably significant corrosion protection compared to some other drugs. Thus, it can be clearly understood that the present drug (Esomeprazole magnesium trihydrate) can be used for corrosion inhibition application with promising results. The higher inhibition efficiency of the investigated drug can be explained on the basis of strong interaction between metal and drug molecules through several polar groups (such as SO_2,C=O), heteroatoms (N, O, S), and aromatic as well as hetero-aromatic rings.

Table 7. A comparative chart listing the performance s of some drugs as corrosion inhibitors drugs

Drug	Metal/alloy	medium	IE%	Reference
Penciillin G	MS	H_2SO_4	73.7	[51]
Penciillin V	MS	H_2SO_4	63.3	[52]
Cefalexin	MS	HCl	67.5	[53]
Ceftriaxone	MS	HCl	90.0	[54]
Cefotaxime	MS	HCl	90.0	[55]
Cefixime	MS	HCl	90.0	[56]
Quinoline	MS	HCl	88.7	[57]
Esomeprazole Mg Tri hydrate	MS	HCl	88.0	Present work

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